Organic Chemistry 10.1 – 10.3

IB Chemistry

Topic 10 – Organic

Resource:

Brown, Ford, HL Chem

Types of Reactant

Saturated	Unsaturated
•Compounds which contain only single bonds •For example: alkanes	•Compounds which contain double or triple bonds •For example: alkenes, arenes
Aliphatics	**Arenes**
•Compounds which do not contain a benzene ring; may be saturated or unsaturated •For example: alkanes, alkenes	•Compounds which contain a benzene ring; they are all unsaturated compounds •For example: benzene, phenol
Electrophile (electron-seeking)	**Nucleophile (nucleus-seeking)**
•An electron-deficient species which is therefor attracted to parts of the molecules which are electron rich •Electrophiles are positive ions or have a partial positive charge •For example: NO_2^+ , H^+ , $Br^{\delta+}$	•An electron-rich species which is therefore attracted to parts of molecules which are electron deficient •Nucleophiles have a lone pair of electrons and may also have a negative charge •For example: Cl^- , OH^- , NH_3

Types of Reaction

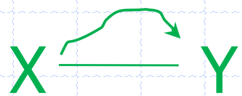
Addition	•Occurs when two reactants combine to form a single product •Characteristic of unsaturated compounds •For example: $CH_4 + Br_2 \rightarrow C_2H_4Br_2$
Substitution	•Occurs when one atom or group of atoms in a compound is replaced by a different atom or group •Characteristic of saturated compounds and aromatic compounds •For example: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
Elimination	•Occurs when a small molecule is lost form a larger compound •Usually results in the formation of a double or triple bond •When the molecule eliminated is H_2O, the reaction is **dehydration** •For example: $C_2H_5OH \rightarrow C_2H_4 + H_2O$
Addition-Elimination	•Occurs when two reactants join together (addition) and in the process a small molecule such as H_2O, HCl or NH_3 is lost (elimination) •Reaction occurs between a functional group in each reactant •Also called **condensation** reaction •For example: $RNH_2 + R`COOH \rightarrow R`CONHR + H_2O$

Types of Bond Breaking (bond fission)

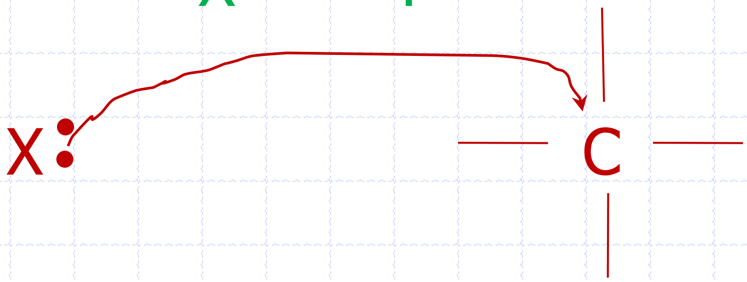
Homolytic fission	Heterolytic fission
•When a covalent bond breaks by splitting the shared pair of electrons between the two products •Produces two free radicals each with an unpaired electron	•When a covalent bond breaks which both the shared electrons going to one of the products •Produces two oppositely charged ions

Convention for depicting organic reaction mechanisms

- Showing movement of electrons
  - Within bonds and between reactants
- The curly arrow is used
  - Drawn from the site electron availability to the site of electron deficiency.



Represents e- pair being pulled towards Y so Y becomes δ- and X becomes δ+



Nucleophile X attracted to e- deficient C

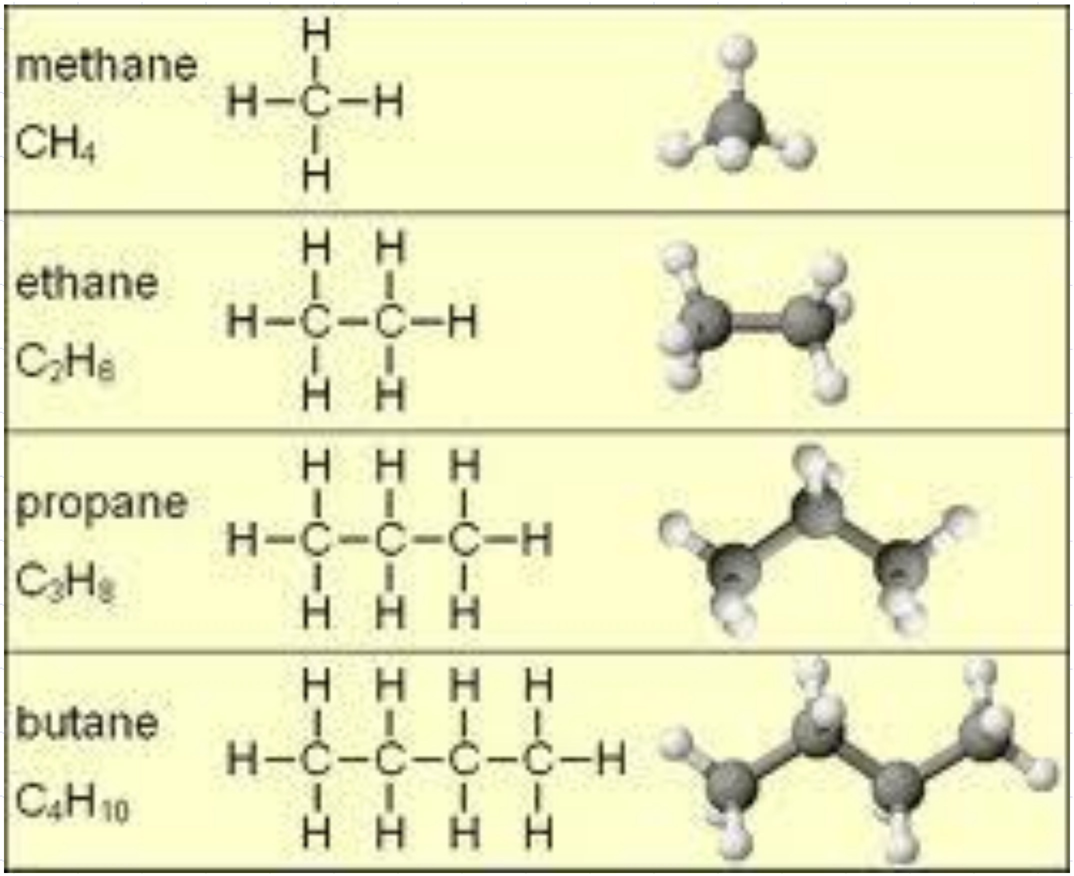
The double-headed arrow represents the motion of an electron pair. When electrons are fully transferred through several steps they are known as the "leaving group."

Members of Homologous Series

- Differ by a CH_2
- Can be represented by the same general formula
- Show gradation in physical properties
- Have similar chemical properties

Members of Homologous Series…

… differ by a –CH_2 group



Members of Homologous Series…

… can be represented by the same general formula

Formula	Name
CH_4OH	Methan-1-ol
C_2H_5OH	Ethan-1-ol
C_3H_7OH	Propan-1-ol
C_4H_9OH	Butan-1-ol
$C_5H_{11}OH$	Pentan-1-ol
$C_6H_{13}OH$	Hexan-1-ol
$C_7H_{15}OH$	Heptan-1-ol
$C_8H_{17}OH$	Octan-1-ol

Members of Homologous Series…

… show gradation in physical properties

Alkane	Boiling Point
Methane, CH_4	-164
Ethane, C_2H_6	-89
Propane, C_3H_8	-42
Butane, C_4H_{10}	-0.5
Pentane, C_5H_{12}	36
Hexane, C_6H_{14}	69
Heptane, C_7H_{16}	98
Octane, C_8H_{18}	125

- Since the series differ by one $–CH_2$ they have successively longer carbon chains
  - Results in gradual trend of phy. Props
  - Not always a linear growth
  - Density and viscosity are other examples

Members of Homologous Series…

… show similar chemical properties

- As the have the same functional group
  - Ex.1 – the alcohols have a functional –OH group, which can be oxidized to form organic acids
  - Ex. 2 – the –COOH functional group, present in the homologous series of the **carboxylic acids**, is responsible for the acidic properties of these compounds

Hydrocarbons

- Hydrocarbons are organic compounds that are made up of only carbon and hydrogen.
- There are several different categories of hydrocarbons including:
  - Alkanes
  - Alkenes
  - Alkynes
  - Cyclic Hydrocarbons
  - Aromatic hydrocarbons

Formulas

- Emperical formula
  - Simplest whole number ratio
  - Ethane CH_3
- Molecular formula
  - Actual number of atoms
  - Ethane C_2H_6
- Structural Formula
  - Full, condensed, steriochemical

Emperical Formula

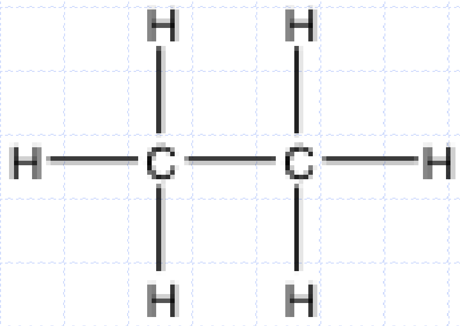
- The simplest whole number ratio of the atoms it contains. For example, the emperical formula of ethane, C_2H_6, is CH_3. This formula can be derived from percentage composition data obtained from combustion analysis. It is, however, of rather limited use on it's own, as it does not tell us the actual number of atoms in the molecule.

Molecular Formula

- Actual number of atoms of each element present. For example, the molecular formula of ethane is C_2H_6. It is therefore a multiple of the emperical formula, and so can be deduced if we know both the emperical formula and the relative molecular mass M_r.

Full Structural Formula

- Graphic formula or displayed formula – shows every bonded atom. Usually 90º and 180º angles are used to show the bonds because this is the clearest 2-D representation, although it is not the true geometry of the molecule



ethane

Condensed Structural Formula

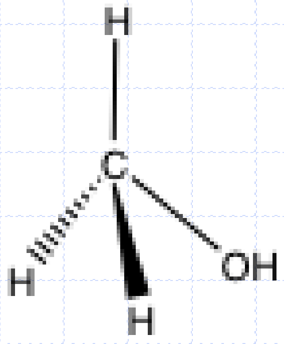
- Often omits bonds where they can be assumed, and groups atoms together. It contains the minimum information needed to describe the molecule non-ambiguously – in other words there is only one possible structure that could be described by its formula.

$$CH_3CH_3$$

ethane

Stereochemical Formula

- Attempts to show the relative positions of atoms and groups around carbon in three dimensions. The convention is that a bond sticking forwards from the page is shown as a solid, enlarged wedge, whereas a bond sticking behind the page is shown as a dotted line. A bond in the plane of the paper is a solid line.



methanol

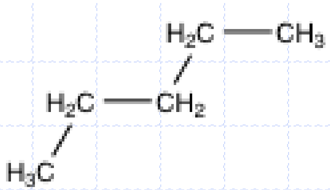
IUPAC

- Nomenclature for Organic Compounds: the IUPAC system
  - International Union of Pure and Applied Chemistry
  - Rule 1: Identify the longest straight chain of carbons
  - Rule 2: Identify the functional group
  - Rule 3: Identify the side chains or substituent groups

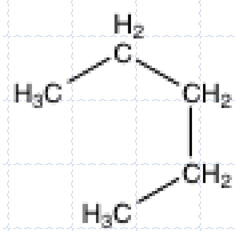
IUPAC Rule 1: Longest Chain

# C atoms in longest	Stem in IUPAC name	Example
1	meth-	CH_4 methane
2	eth-	C_2H_6 ethane
3	prop-	C_3H_8 propane
4	but-	C_4H_{10} octane
5	pent-	C_5H_{12} pentane
6	hex-	C_6H_{14} hexane

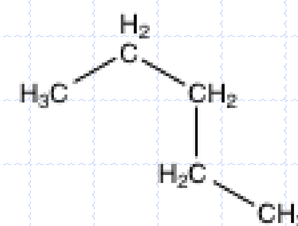
Note: 'straight chain' does not mean just 180^{o} angles or unbranched chains of carbon atoms. Be careful, do not be confused by the way the molecule may appear on paper because of free rotation around the carbon-carbon single bonds. Example, all three below are the same….



pentane



pentane

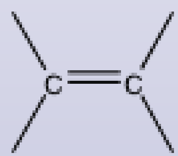
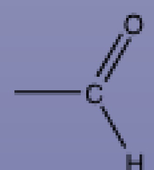


pentane

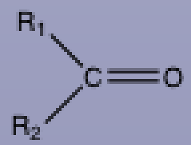
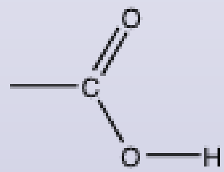
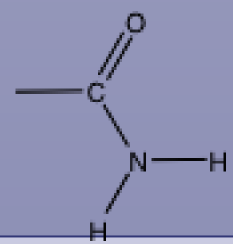
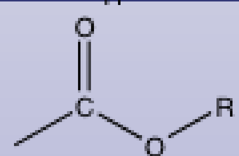
IUPAC Rule 2: Functional Group

- The functional group is described by a specific ending (or suffix) to the name, that replaces the –ane ending of the name of the parent alkane. The suffixes used for some common functional groups are in the slides to follow. Those marked * will have slides with further information.

Functional Groups

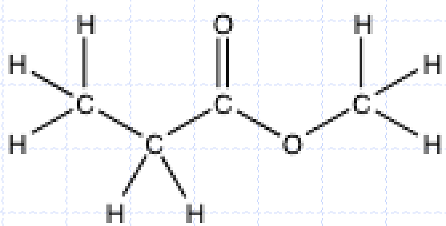
Homologous Series	Functional Group	Suffix in IUPAC name	Example of compound
Alkane		-ane	C_3H_8 propane
Alkene		-ene	$CH_3CH{=}CH_2$ propene
Alcohol	—OH	-anol	C_3H_7OH propanol
Amine*	—NH_2	-anamine	$C_3H_7NH_2$ propanamine
Aldehyde		-anal	C_2H_5CHO

Functional Groups

Homologous Series	Functional Group	Suffix in IUPAC name	Example of compound
Ketone		-anone	CH_3COCH_3 propanone
Carboxyllic acid		-anoic acid	C_2H_5COOH Propanoic acid
Amide*		-anamide	$C_2H_5CONH_2$ propanamide
Ester		-anoate	$C_2H_5CHOH_3$ methyl propanoate
Nitrile (HL)		-anenitrile	C_2H_5CN propanenitrile

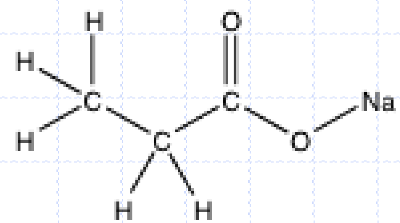
Ester Functional Group

- Esters are organic salts where the alkyl group of the alcohol has replaced the hydrogen of the carboxylic acid. Their name puts the alkyl group first followed by the name of the acid anion, for example:



methyl propionate

$C_2H_5COOCH_3$



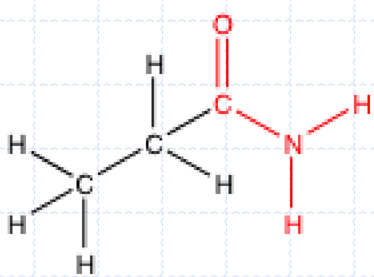
sodium propionate

C_2H_5COONa

Amide Functional Group

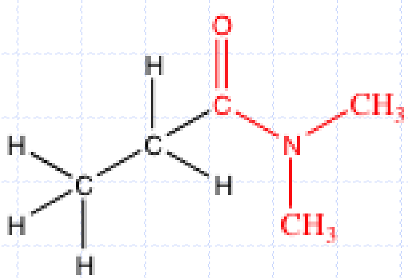
- Amides are acid derivatives where the –OH of the acid has been replaced by $–NX_2$. Primary amides have an $–NH_2$ group; secondary and tertiary amides are substituted with respectively one and two alkyl groups bonded to the nitrogen. In these cases the substituent groups are nemed usning N- and N,N- before the substituent.

Primary amide..



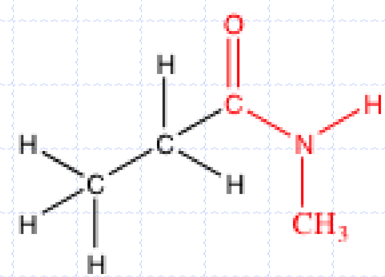
propionamide

Tertiary amide..



N,N-dimethylpropionamide

Secondary amide..

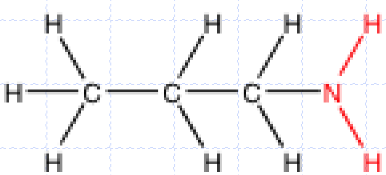


N-methylpropionamide

Amine Functional Group

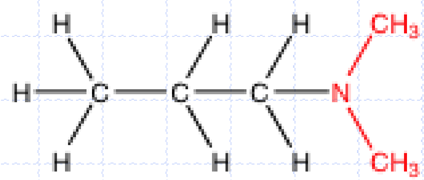
- Primary amines have an $-NH_2$ group which can undergo substitution by alkyl groups, giving rise to secondary and teriary amines. These are named in a similar way to the amides, using N- to show the position of the substituents

Primary amine..



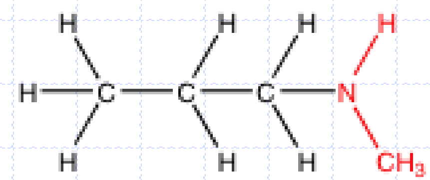
propan-1-amine

Tertiary amine..



N,*N*-dimethylpropan-1-amine

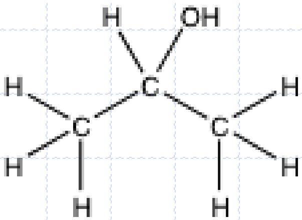
Secondary amine..



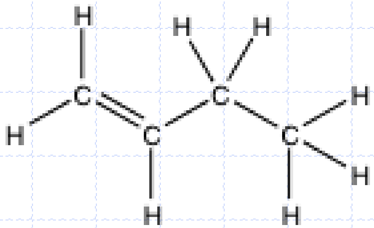
N-methylpropan-1-amine

Position of Functional Group

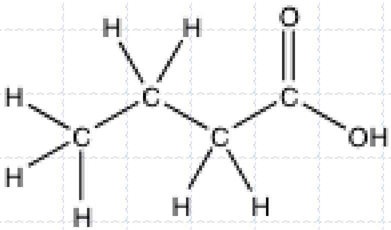
- Shown by a number between hyphens inserted before the functional group ending. The number refers to the carbon atom to which the functional group is attached when the chain is numbered starting at the end that will give the smallest number to the group.



propan-2-ol

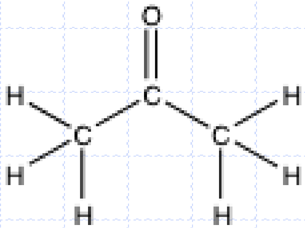


but-1-ene



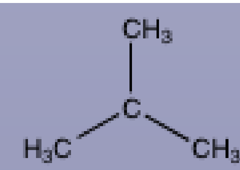
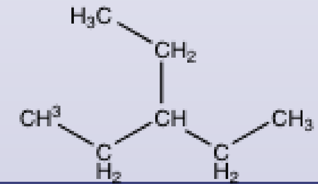
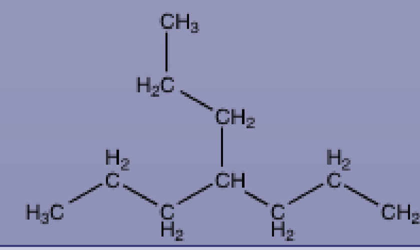
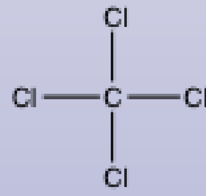
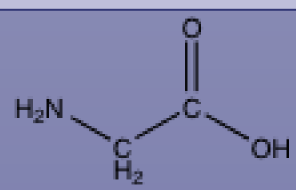
butyric acid

aka, butanoic acid



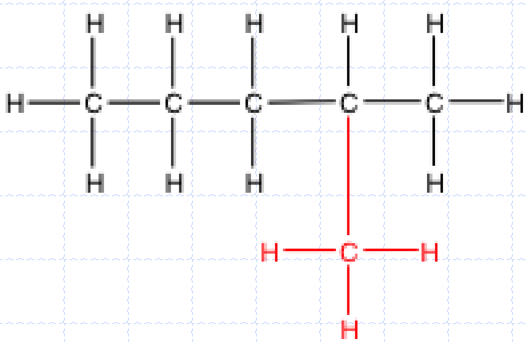
propan-2-one

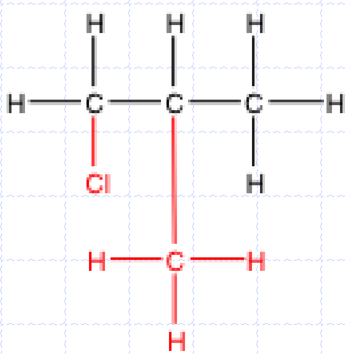
IUPAC Rule 3: Side Chains

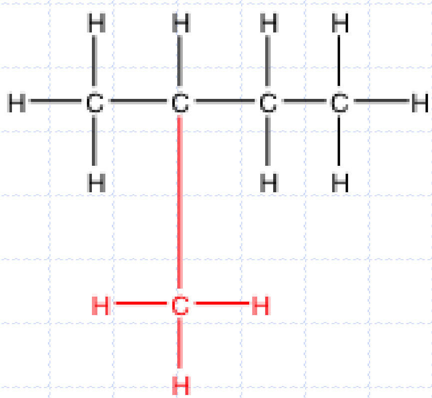
Side Chain	Prefix in IUPAC	Example of Compound	
$-CH_3$	methly-	$CH_3CH(CH_3)CH_3$ 2-methylpropane	
$-C_2H_5$	ethly-	$CH(C_2H_5)_3$ 3-ethlypentane	
$-C_3H_7$	proply-	$CH(C_3H_7)_3$ 4-propylheptane	
-F , -Cl , -Br , -I	fluoro- , chloro- , bromo- , iodo-	CCl_4 Tetrachloromethane	
$-NH_2$	amino-	$CH_2(NH_2)COOH$ 2-aminoethanoic acid	

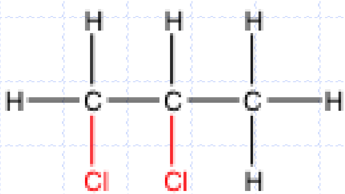
When >1 functional group

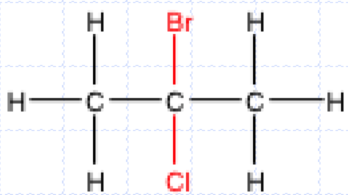
- Some suffix's may become prefix's
  - $-NH_2$ can be amino- prefix or –amine suffix
- If more than one of the same functional group we use prefixes di-, tri-, tetra- before the name


2-methylpentane


2-bromo-2-chloropropane

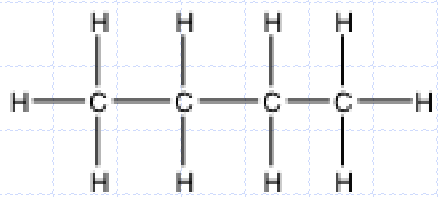

2-methylbutane


1,2-dichloropropane

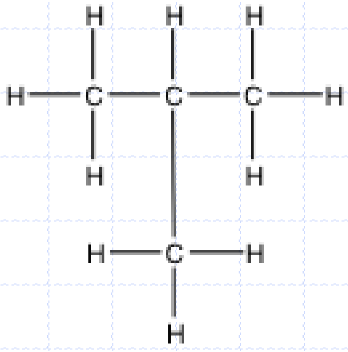

1-chloro-2-methylpropane

Structural Isomers

- Different arrangements of the same atoms make different molecules
- Molecular formula shows the atoms that are present in a molecule, but gives no information on how they are arranged. Consider, for example, C_4H_{10}
- Each isomer is a distinct compound, having unique physical and chemical properties.

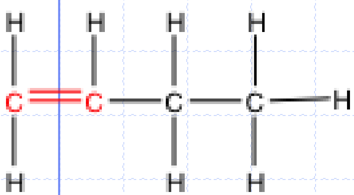


butane
boiling point -0.5^{o}c

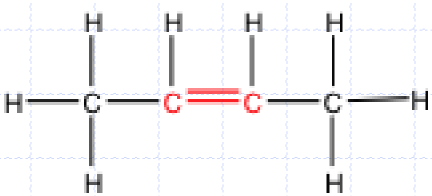


2-methyl propane
boiling point -11.7^{o}c

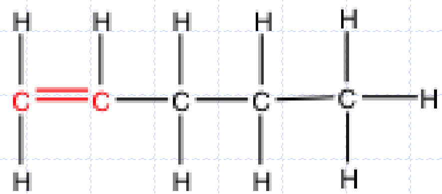
Structural Isomers of Alkenes



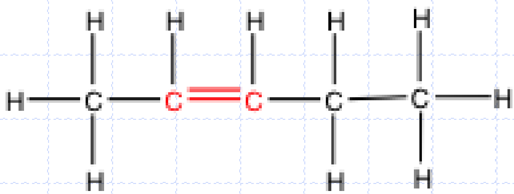
but-1-ene



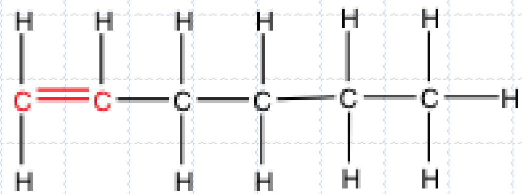
but-2-ene



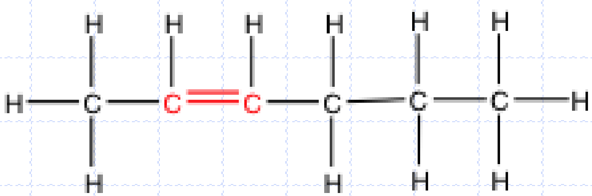
pent-1-ene



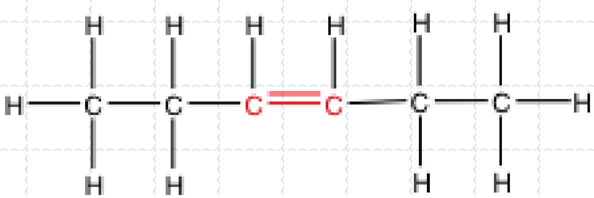
pent-2-ene



hex-1-ene



hex-2-ene



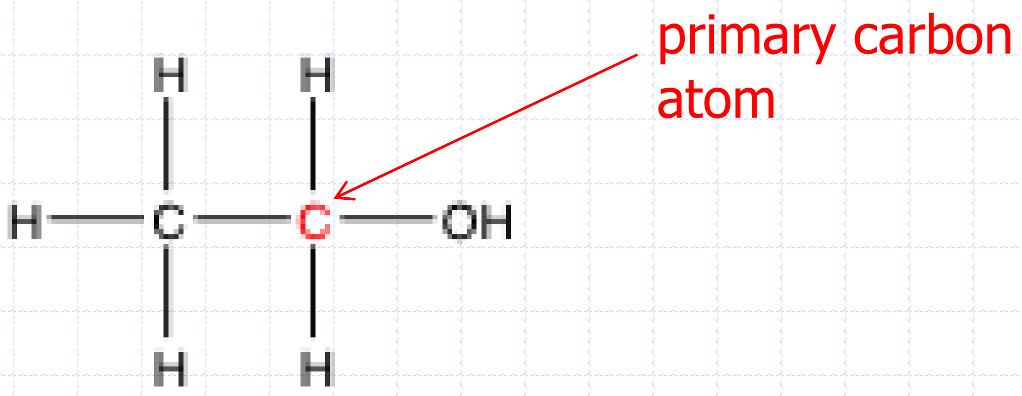
hex-3-ene

Classes of Compounds

- The activity of a functional group is often influenced by its position in the carbon chain, identified as:
  - Primary carbon atom
  - Secondary carbon atom
  - Tertiary carbon atom

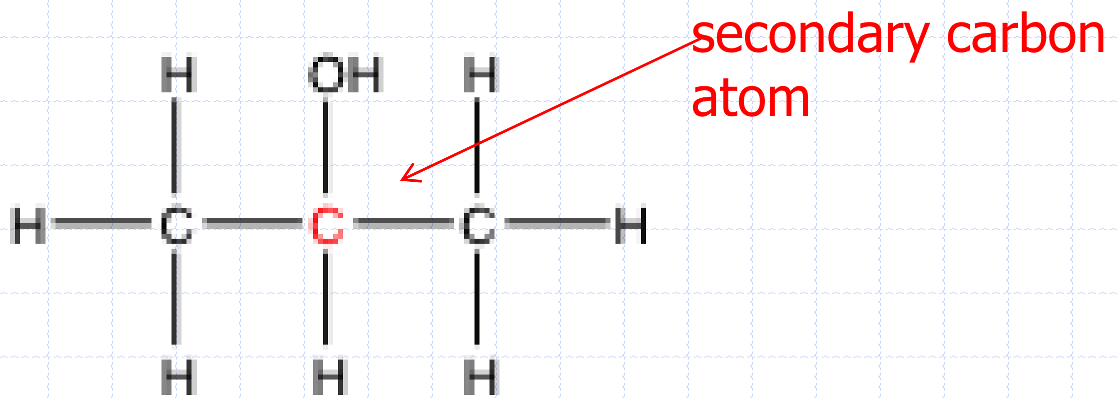
Primary Carbon Atom

- Is attached to the functional group and also to at least two hydrogen atoms. Molecules with this arrangement are known as primary molecules.
- For example, ethanol C_2H_5OH is a primary alcohol:



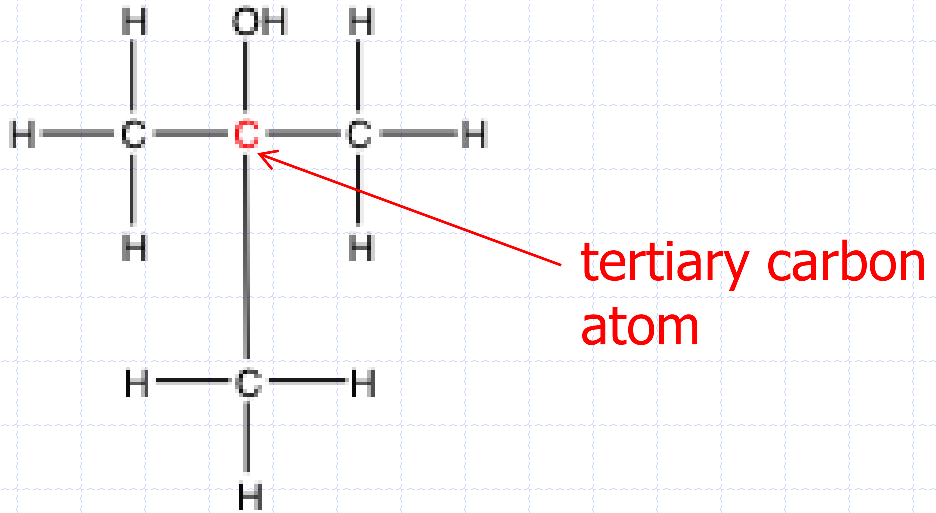
Secondary Carbon Atom

- Is attached to the functional group and also to one hydrogen atom and two alkyl groups. These molecules are known as secondary molecules
- For example, propan-2-ol, $CH_3CH(OH)CH_3$ is a secondary alcohol:



Tertiary Carbon Atom

- Is attached to the functional group and is also bonded to three alkyl groups and so has no hydrogen atoms. These molecules are known as tertiary molecules.
- For example, 2-methylpropan-2-ol, $C(CH_3)_3OH$ is a tertiary alcohol:



Trends in Physical Properties

- We have seen that the structure of organic compounds can be thought of in terms of two parts
  1. A framework consisting of carbon and hydrogen only, known as the **hydrocarbon skeleton**. This differs in size in different members of the same homologous series.
  2. A functional group. This differs in identity in different homologous series.
- Both of these components influence the physical properties of a compound and must each be considered when comparing properties such as volatility and solubility in water

Volatility of Organics

- Volatility: a measure of how easily a substance changes into the gaseous state – highly volatile means the compound has a low boiling point.

Hydrocarbon Length effect on Volatility

- Higher members have larger molecules and stronger van der Waals’ forces between them.
- Boiling Point increases ⇧.
- Lower members gases (g) or liquids (l)
- Higher likely solids (s)
- Branched chain isomers have lower boiling points (and intermolecular attractions) than straight-chain isomers.

Functional Group effect on Volatility

- Polar groups develop dipole-dipole interactions with neighboring molecules which raise the boiling point.
- For example:
  - Ethanol C_2H_5OH $M_r=46$ BP=78°c
  - Propane C_3H_8 $M_r=44$ BP=-42°c

The effect on volatility of the different functional groups as follows:

Most Volatile ... Least Volatile

alkane > halogenalkane > aldehyde > ketone > alcohol > carboxylic acid

van der Waals' → dipole-dipole interaction → hydrogen bonding

Increasing strength of molecular interaction →

Increasing boiling point →

Solubility in Water

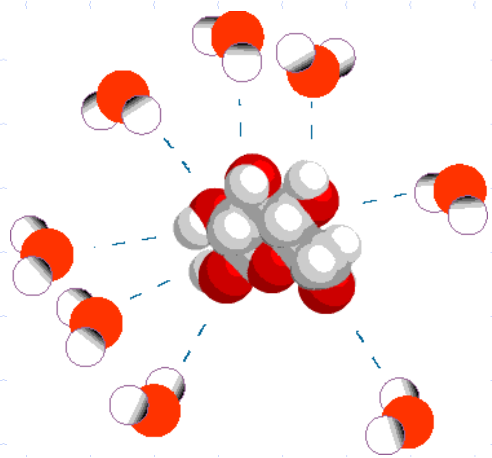
- Solubility is largely determined by the extent to which the solute molecules are able to interact and form hydrogen bonds with water. Depends once again on:
  - Hydrocarbon skeleton
  - Functional Group

Hydrocarbon Chain Effect on Solubility

- As this part of the molecule is non-polar and unable to form hydrogen bonds with water, it does not contribute to the solubility of the molecules. Therefore, higher members of all homologous series are less soluble than lower members

Functional Group effect on Solubility

- Molecules with functional groups that enable hydrogen bonds to form with water include **alcohols**, the **carboxylic acids** , and the **amines**. Aldehydes, ketones, amides and esters are less soluble, while halogenalkanes, alkanes and alkenes are insoluble.



Alkanes

- Alkanes contain only C-C and C-H bonds and are both strong so only react in the presence of a strong source of energy
  - C-C, 348 kJ/mol
  - C-H, 412 kJ/mol
  - Can be stored, transported, and compressed safely which is why they are so useful
  - C-H, C-C bonds are characteristically non-polar so are not susceptible to attack by most common reactants.

Alkanes as Fuels

- Release significant amounts of energy when they burn, highly exothermic, because large amount of energy released when forming..
  - Double bonds of CO_2
  - Bonds in H_2O

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H = -2200\ kJ/mol$$

However, when O_2 is limited.....

$$2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O$$

when O_2 is extremely limited.....

$$C_3H_8 + 2O_2 \rightarrow 3C + 4H_2O$$

These are examples of the incomplete combustion of fossil fuels which makes them an environmental concern

Halogenation of Alkanes

- Saturated compounds, the main type of reaction they can undergo is **substitution**
- Occurs when another reactant (Halogen), take the place of a hydrogen atom in the alkane
- For example, methane CH_4, reacts with chlorine Cl_2 producing chloromethane and hydrogen chloride
- Cannot take place in the dark, as the UV light is necessary to break the covalent bond.
- Splits chlorine, Cl_2, into **free radicals** and the chain reaction begins…

Halogenation of Alkanes

UV light

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Part I - Initiation:

Homolytic Fission because the bond between the two Chlorine atoms is broken, splitting the shared pair of electrons between two atoms. Homo- means "the same" and refers to the fact that the two products have equal assignment of electrons from the bond.

$Cl_2 \rightarrow$ 2Cl• radicals

Halogenation of Alkanes

UV light

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Part II - Propagation:

Called such because they both use and produce free radicals, and so allow the reaction to continue. This is why the reaction is often called a chain reaction.

$$Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

$$CH_3Cl + Cl\bullet \rightarrow CH_2Cl\bullet + HCl$$

$$CH_2Cl\bullet + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$$

Halogenation of Alkanes

UV light

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Part III - Termination:

These reactions move free radicals from the mixture by causing them to react together and pair up electrons.

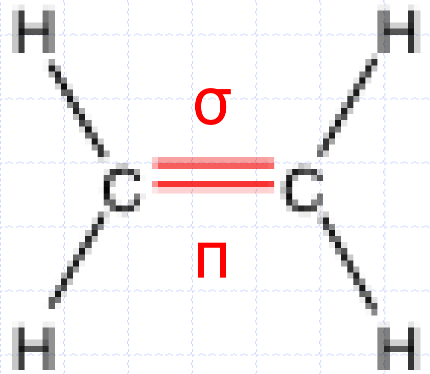
$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$

Alkenes

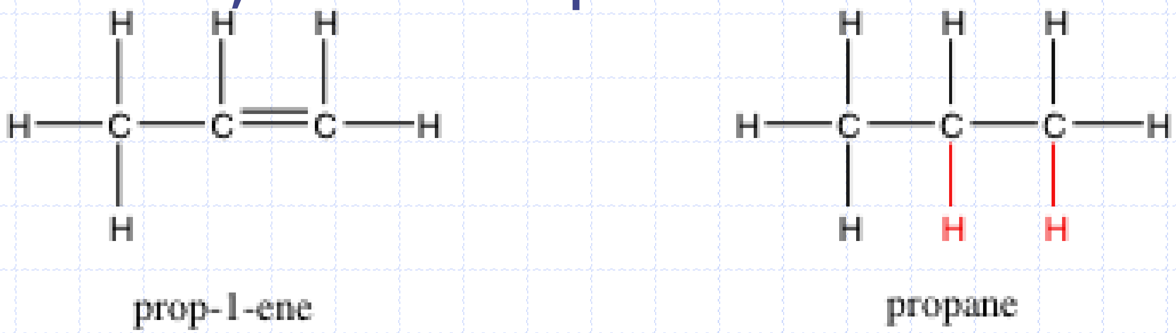
- General formula is C_nH_{2n}
- Alkenes are **unsaturated hydrocarbons** containing a carbon-carbon double bond



  - Double bond is made of two types of bonds, one sigma σ, and one pi π. Carbon atoms are sp^2 hybridized, forming a trigonal planar arrangement of groups with 120^o angles

Alkene addition with Hydrogen

- With the presence of a nickel catalyst at about 150°c, for example



$$CH_3CHCH_2 \quad + \quad H_2 \quad \text{---->} \quad CH_3CH_2CH_3$$

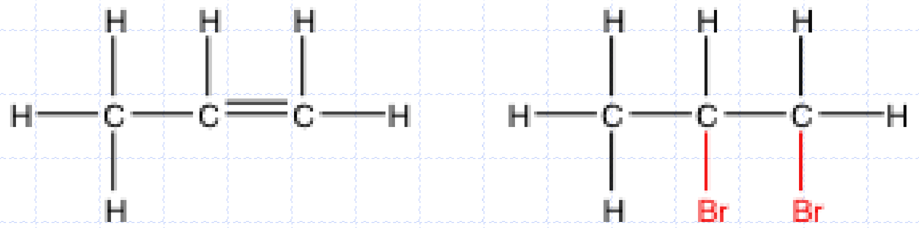
Ni catalyst

propene   hydrogen gas   propane

- Known as **hydrogenation**, used in the margarine industry to convert oils containing unsaturated hydrocarbon chains into more stable saturated compounds with higher melting points

Alkene addition with halogens

- Halogens react with alkenes to produce dihalgeno compounds.
- Occur quickly at room temperature and are accompanied by the loss of color of the reacting compound.



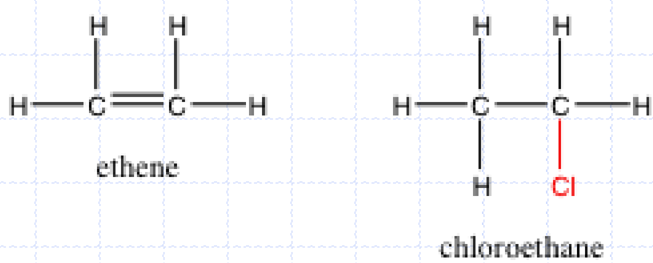
prop-1-ene 1,2-dibromopropane

CH_3CHCH_2 + Br_2 ----> $CH_3CHBrCH_2Br$

propene bromine gas 1,2-dibromopropane

Alkene addition with hydrogen halides

- Hydrogen halides (HCl, HBr, etc) react with alkenes to produce hydrogenalkanes.
- Take place rapidly in solution at room temperature.
- All halogens are able to react in this manner, but the reactivity is in the order HI>HBr>HCl, per the decreasing strength of the hydrogen halide bond.

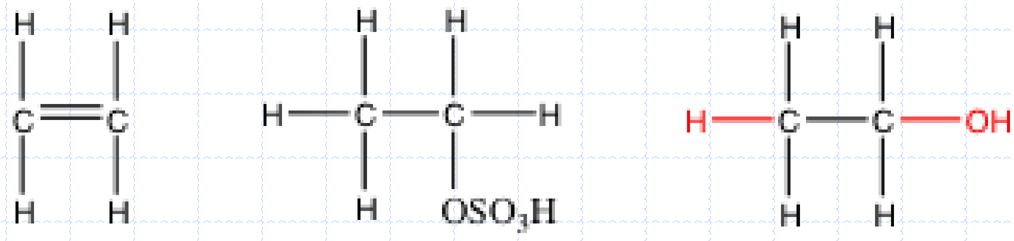


CH_2CH_2 + HCl ----> CH_3CH_2Cl

ethene chloroethane

Alkene addition with water

- The reaction with water is known as hydration and converts the alkene into an alcohol.
- Use of concentrated sulfuric acid as catalyst.
- Involves intermediate in which H^+ and HSO_4^- ions are added across the double bond.



ethene ethyl hydrogen sulfate ethanol

$$CH_2CH_2 \xrightarrow{H_2SO_4\,(conc)} CH_3CH_2(HSO_4) \xrightarrow{H_2O} CH_3CH_2OH + H_2SO_4$$

ethene ethyl hydrogen sulfate ethanol

Distinguish between Alkanes and Alkenes

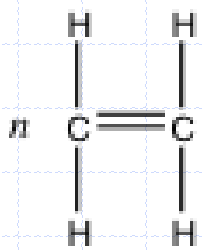
- Alkenes readily undergo addition reactions, alkanes will not (and only in UV light)
- Shake separate samples of alkanes and alkenes with bromine water at room temperature, red-brown color of bromine water is decolorized by the alkene (but not the alkane)
- Color of a burned flame. Alkenes have high ratio of C:H and leave unburned carbon. Results in a smokier, dirtier flame from alkenes.

Polymerization of alkens

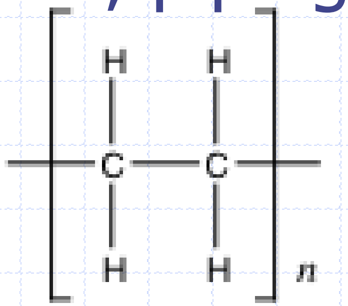
- Since alkenes readily undergo addition reactions by breaking their double bonds, they can be joined together to produce long chains known as **polymers**. The alkene is known as the **monomer**.
- Example:
  - Ethene polymerizes to form polyethene, commonly known as **polythene**. First discovered by accident in 1935, was used extensively as an insulator in the WWII.

Repeating Units for Polymers

- Polythyene:
  - Insulator, water tanks, piping..

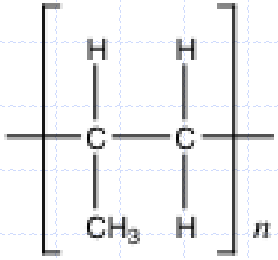


ethene



the repeating unit

- Polypropylene:
  - Manufature clothing, especially thermal wear



the repeating unit

PVC (poly vinyl chloride)

- Polychloroethane (PVC) is widely used in construction materials, packaging, electrical cable sheathing, etc.
- Synthesis is associated with toxic byproducts known as **dioxins**, which are linked to reproductive disorders and a variety of cancers.